A Random Walk through Time and Space

Random motion rules from the smallest molecules to the largest meteorological events, with enormous results.

IN 1905, Albert Einstein published five papers that shook the world of physics. His elegant arguments and conclusions were marvels of physical intuition that addressed dilemmas raised by experimental evidence. Those papers have been so important to physics research that 1905 is known as Einstein's miraculous year.

One of the papers, "On the Movement of Small Particles Suspended in Stationary Liquids Required by the Molecular-Kinetic Theory of Heat," has profoundly affected how scientists view the makeup of physical matter. In that paper, Einstein combined kinetic theory and classical thermodynamics, laying the theoretical groundwork for measurements to confirm the existence of atoms. Later that year, he extended his mathematical development of the theory, writing "On the Theory of Brownian Motion," which was published in February 1906.

In addition, he submitted his doctoral dissertation on the size of molecules. One of Einstein's most frequently cited papers, it shows how to use fluid phenomena to determine Avogadro's number—the number of atoms in a defined mass of material.

The work underlying these three publications embraced a branch of physics known as statistical mechanics and helped confirm the atomic theory of matter. A century later, it continues to form the basis for much of the Laboratory's work in molecular dynamics, Monte Carlo statistical techniques, and physical chemistry.

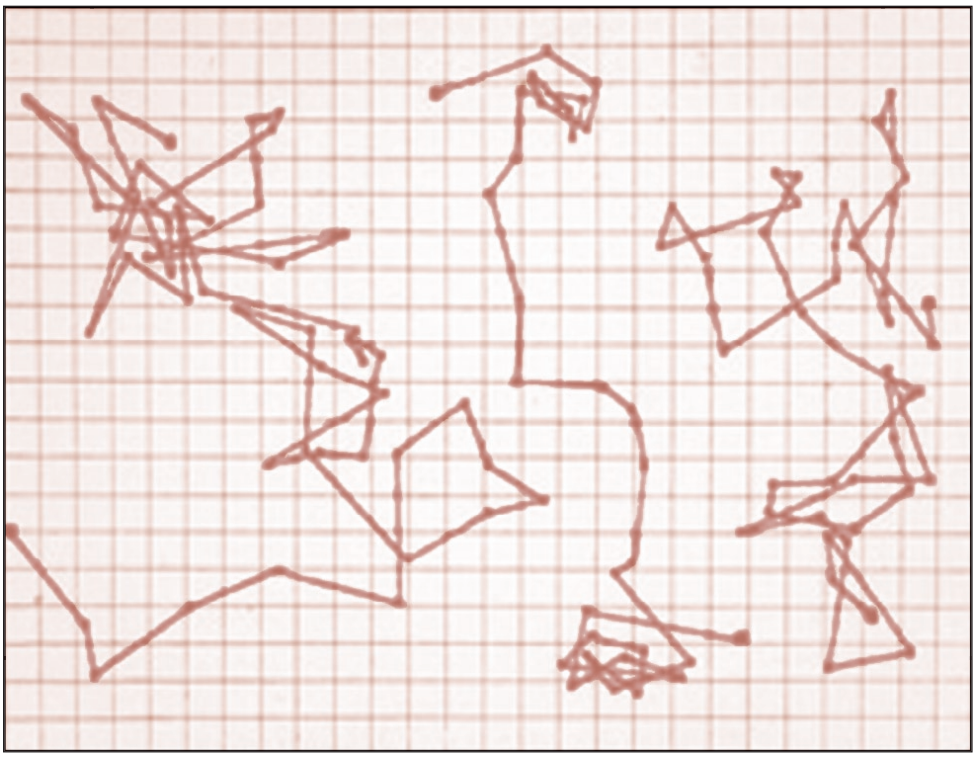
The Molecular Dance

The story of Brownian motion begins long before Einstein's time. In the summer of 1827, the botanist Robert Brown noted that when pollen grains suspended in water were viewed through a microscope, they appeared to be dancing as if they were alive. Brown showed that this motion occurred whenever such small particles—living or nonliving—were suspended in water. The movement neither slowed nor stopped, but it was affected by the temperature of the liquid in which the particles were suspended.

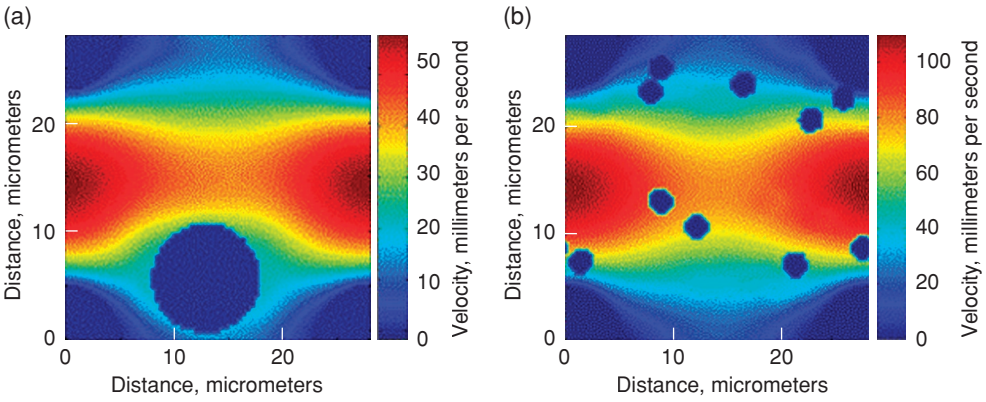
At the time, many scientists suspected this random motion had to do with molecular movement, but no one could explain it quantitatively until Einstein published his 1905 paper. In so doing, he managed to reconcile the laws of thermodynamics—the mechanical actions of heat flow—with the kinetic theory of gases.

The first law of thermodynamics relates heat, energy, and useful work to each other in thermal processes. If all matter consists of atoms or molecules, then heat is the energy of motion—the kinetic energy—of these atoms. The first law, which is

basically conservation of energy, states the reversibility of physics and could be understood in terms of the motions and collisions of Newtonian atoms. A movie showing collisions between simple atoms looks normal if run backward. The second law of thermodynamics defines the flow of heat in natural processes, such as the melting of ice. This law is irreversible: Ice that has melted at room temperature will not refreeze by itself.



Albert Einstein's papers on Brownian motion led French scientist Jean Perrin to record the irregular motion of suspended particles in a solution.



The lattice Boltzmann code characterizes fluid flow and filtration, using the generalized Einstein equation to study hindered transport phenomena. These examples show results from the characterization of (a) hindered convection and (b) species capture in a regular array of cylinders.

Faced with the paradox that interactions are reversible and nature is irreversible, some scientists chose to deny the existence of atoms. Two physicists, James Clerk Maxwell and Ludwig Boltzmann, approached the issue by building on the 18th-century idea that matter, such as a volume of gas, is composed of many tiny particles. Boltzmann, in particular, resolved the contradiction between Newtonian mechanics and thermodynamics by interpreting the second law as a statistical law, not an absolute. Many results of thermodynamic experiments, he said, could be explained by calculating the average or statistical behavior of such a collection of particles.

Of Random Walks and Statistics

Einstein's doctoral dissertation developed a statistical molecular theory of liquids. (See the box on p. 15.) In his subsequent 1905 paper, he predicted that randomly moving molecules in liquid impact larger suspended particles, causing them to move randomly. He derived a relation between how far these particles jiggled over time and the temperature, the liquid's viscosity, the number of molecules in the liquid, and their size. Knowing this mathematical relationship, Einstein reasoned, scientists could then measure the size and number of the molecules in a liquid using a microscope and a stopwatch. A few years later, French physicist Jean Perrin and his students conducted such an experiment, and by 1913, most physicists accepted the atomic theory of matter.

Einstein's work on Brownian motion also was the first practical application of random processes for understanding physical phenomena, because he related the random walk of a single particle to the diffusion of many particles. This randomness was the source of the irreversibility of many macroscopic

processes and, hence, the second law of thermodynamics.

Studies of these processes were just beginning in 1905. Today, many projects at Lawrence Livermore reflect back to Einstein's seminal work on Brownian motion, random processes, and statistical mechanics. These projects all build on Einstein's legacy, from understanding biological functions and simulating the movement of molecules and individual atoms in plutonium, to using Monte Carlo techniques for atmospheric predictions and discovering the existence of a low-temperature quantum fluid in hydrogen.

Statistically Speaking of Fluids

In one project, Livermore engineer David Clague leads an effort to develop computational tools for statistically studying fluid behavior. These simulations do not track individual molecules; instead, they represent the collective behavior of fluid molecules in different regions. One of these models includes a generalized Einstein equation to study hindered transport phenomena. "Basically," says Clague, "we're simulating how very small particles—from nanometers to micrometers in diameter—move through fluids and filtrate or pass through a barrier."

Clague's team has modeled the process of kidneys filtering out contaminants and microfluidic systems designed to capture and analyze pathogenic particles. The three-dimensional (3D) transport model is based on the lattice Boltzmann (LB) equation. This equation statistically describes the fluid as a cubic lattice, where each lattice site represents up to several thousand individual fluid molecules. Developed with funding from Livermore's Laboratory Directed Research and Development (LDRD) Program, the LB model incorporates external forces and structures such as biological membranes or porous glass to study thermal diffusion and the dynamic behavior of a collection of particles.

Clague is working with Kevin Ness, a doctoral student from Stanford University, on a multiphysics version of the LB model. This code includes detailed descriptions of microstructures, the relevant surface forces that characterize microstructure capture and release of specific species such as types of DNA, and the temperature effects for both liquid- and gas-phase systems. The simulations use complicated 3D models of actual materials rather than idealized models of materials. Ness is using the multiphysics code to model hindered transport on a microfluidic chip that has small glass pillars designed to capture DNA for analysis.

The multiphysics code also contains modules that can create a complete picture of how particles flow in liquids or gases, and it works with both natural and manufactured materials. "It even works with physiological media," says Clague. "It's all about diffusion, which takes us right back to Einstein and his work."

Zeroing In on Atmospheric Releases

In another LDRD project, Livermore physicist Branko Kosovic and engineer Bill Hanley are developing a computational tool to help scientists at Livermore's National Atmospheric Release Advisory Center better predict the consequences of hazardous releases to the atmosphere, which is particularly challenging when the source of the release is unknown or poorly characterized.

Atmospheric dispersion is complex and difficult to reconstruct. For instance, an explosion releases contaminants instantaneously, but a forest fire spews them out continuously. Contaminants also may be static or moving, and they may be released near Earth's surface or at elevated altitudes. In addition, atmospheric conditions such as wind direction, velocity, and turbulence affect their movement.

The Livermore-developed reconstruction capability rests on Bayesian inference, a probabilistic approach that combines observed data, physical models, and prior knowledge. The result is a sample of likely dispersion scenarios given what is known thus far. When all of the observed data are available up front, the event reconstruction uses Markov chain Monte Carlo (MCMC) to sample the dispersion scenarios, including the possible location of the emitting source.

His Thesis Lives On

In his doctoral thesis, Albert Einstein used statistical mechanics (the study of the motion of objects using mathematical tools for dealing with large numbers of objects) to estimate the size of molecular radii and how many molecules would be found in a fixed amount of material.

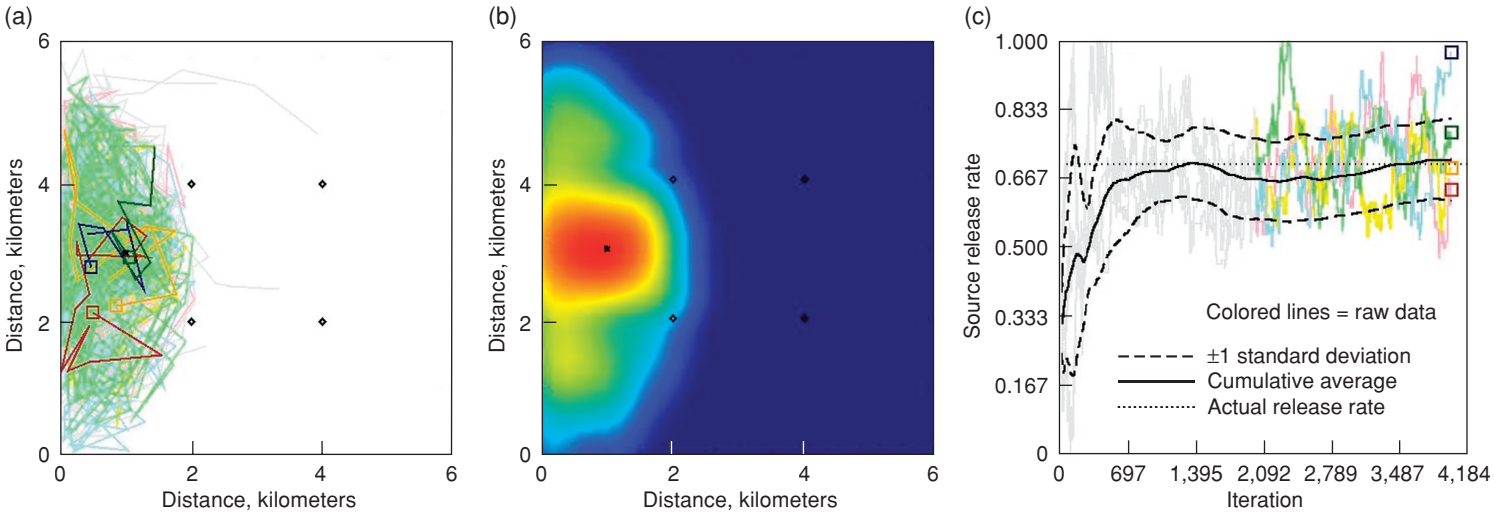
At that time, the existence of molecules and atoms had not been definitively established. In his thesis, Einstein used atomic theory to explain how substances such as sugar would dissolve into water. He related the diffusion coefficient (the measure of how quickly materials diffuse in a liquid) to the temperature, number of atoms, viscosity of the liquid, and the size of the atoms dissolving into the liquid. This fundamental relation is now known as the Einstein equation. Using values of the diffusion coefficient and viscosity obtained from experiments done at fixed temperatures, Einstein related the total number of atoms in the liquid to the size of the sugar molecules. Einstein also showed that the liquid's viscosity depended on how much volume was taken up by the dissolved material.

Of all Einstein's work in 1905, his thesis had the most practical applications. The techniques he employed have been used to explain the motion of sand particles in concrete mixes, protein blobs in milk, and aerosol particles in clouds.

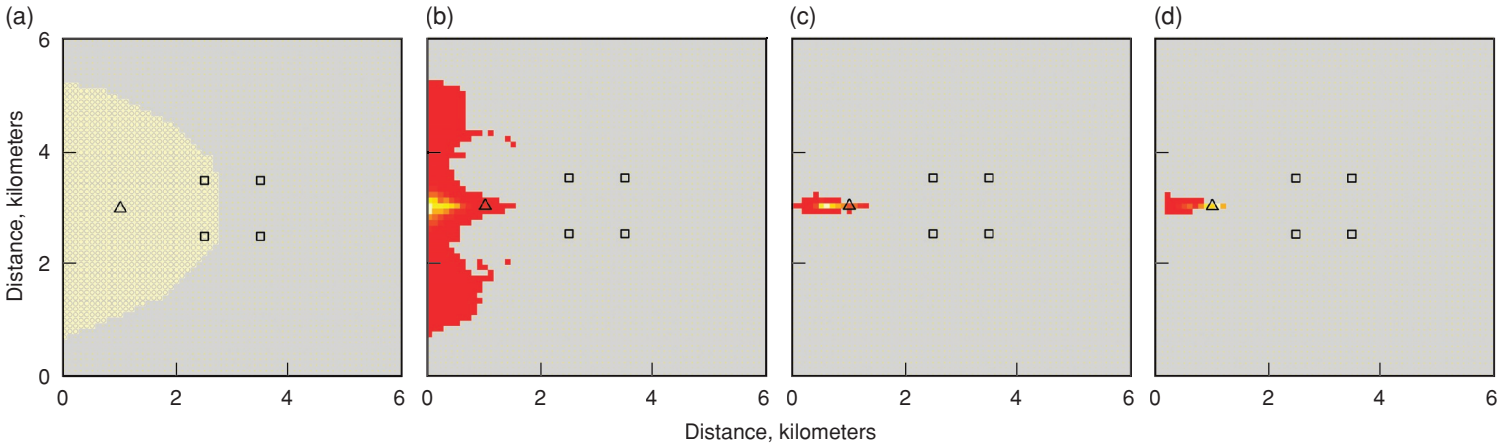
In a more dynamic setting, where the data are accumulated over time as the event unfolds, the reconstruction relies on a sequential Monte Carlo (SMC) sampling approach.

"MCMC is a proven technique that typically uses a random-walk-type procedure to sample possible outcomes when given all the available data up front," says Hanley. "However, MCMC is inefficient and costly when the goal is to dynamically update the pool of possible outcomes as more data become available. The SMC sampling approach was developed to handle those cases. It reweights and resamples the current pool of possible outcomes to reflect the newly available data in an efficient way."

Statistical theory and the related science-based application tools seem a long way from Einstein's original papers. Yet, in some ways, they are direct descendants from his work. "As the problems of event reconstruction get



(a) In a random walk reminiscent of Perrin's 1908 recordings of particles in a fluid, a two-dimensional code does a statistical dance to reconstruct the characteristics of a hypothetical atmospheric release based on concentrations measured by four sensors in a square array. This feasibility demonstration started with a square sensor array and uses Monte Carlo statistics to deliver a probabilistic determination of (b) the source location and (c) the release rate.



Using sequential Monte Carlo for atmospheric event reconstruction allows the code to dynamically update its calculations as more data are gathered over time. In this two-dimensional example, the release starts after a 10-minute interval, with an exponentially decaying release rate over the next 50 minutes. Data are gathered at 10-minute intervals. (a) The initial conditions, before stochastic sampling begins, are used to set the source term parameters (given the wind direction, we know the source is not located to the right of the sensors). The probability distribution for source location is shown after (b) 20 minutes, (c) 40 minutes, and (d) 60 minutes of data gathering and code calculations. Each color represents a 10-percent probability mass, where red is low probability and yellow is high.

increasingly complex and uncertain, we need proven computational models to handle uncertainties whether they stem from changing meteorological conditions or unknown variables in the data we've collected," says Kosovic. "The stochastic methodologies introduced by Einstein and others are adaptable to many dynamic systems. It's just the beginning for us."

Seeing Atoms

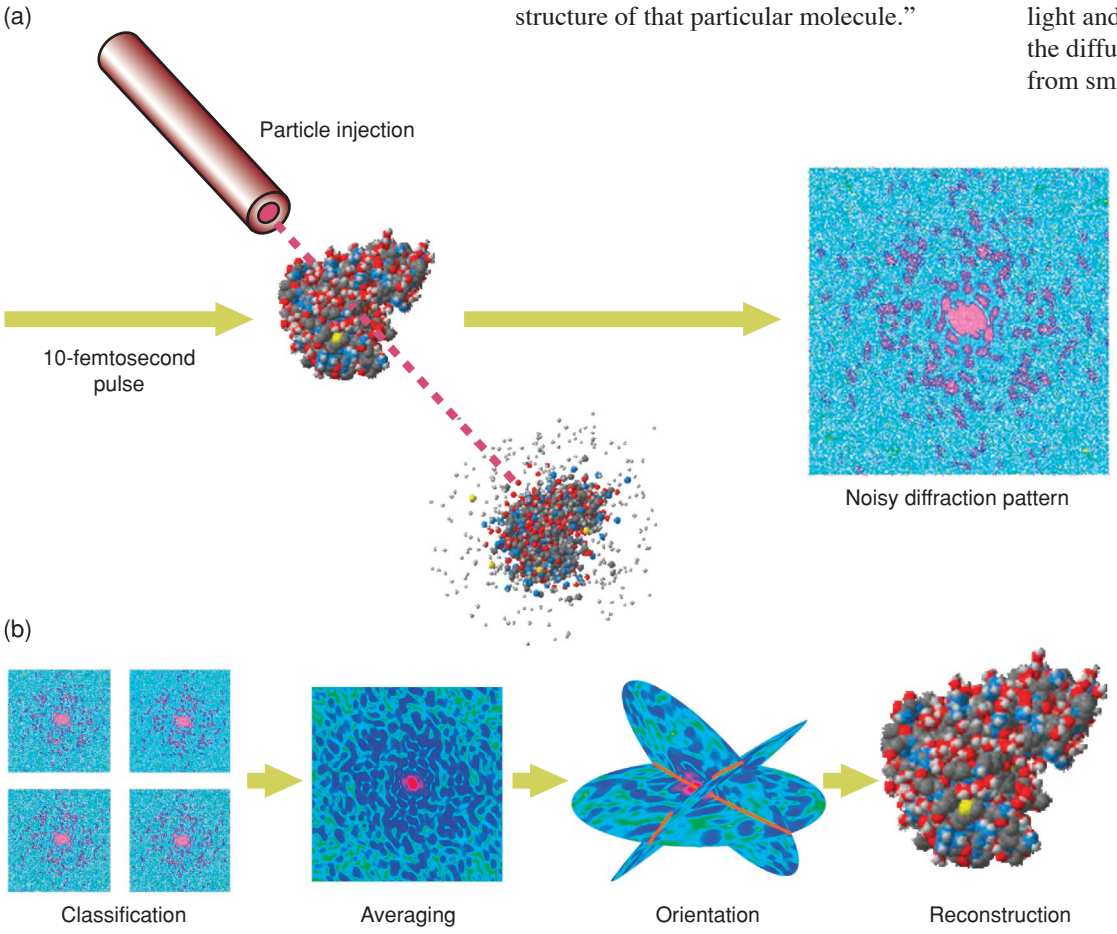
The scientists of Einstein's day had no hope of seeing atoms, but a century later, new technologies are making that a reality. Livermore physicists Henry Chapman and Stefan Hau-Riege received LDRD funding for their work on a project that will use the Linac Coherent Light Source at the Stanford Linear Accelerator Center to image complex biological molecules composed of 10,000 to 100,000 atoms. (See *S&TR*, September 2000, pp. 23–25; December 2003, pp. 4–10.) "We've moved in the space of a century from discussing whether atoms exist to actually being able to image atoms in crystals," says Chapman, "and we're on the threshold of imaging them in noncrystalline biological macromolecules, protein complexes, or viruses."

The basic technique for constructing these images is to inject a single molecule into the path of an incoming x-ray pulse and then measure the resulting diffraction pattern—the pattern of scattered x rays just before the molecule explodes from energy absorbed. "One image doesn't give us a full 3D picture of the molecule, so we repeat the process many times," says Hau-Riege. "We combine data from all of the images to build a 3D model of the molecule, which gives us an average structure of that particular molecule."

Although the same type of molecule is being imaged each time, the diffraction patterns differ. "Brownian motion is partly to blame," says Chapman. "The molecules are jiggling and so are the atoms. Atoms also have thermal vibration, and even though they're bonded to each other, they're moving about. Some even swing at the end of their bonds, like a tether ball." To resolve this problem, the team is developing methods to align the molecules so they will always have the same orientation when imaged.

Looping the DNA Loop

In 1908, Perrin's team used microscopes to view particles one-thousandth of a millimeter in diameter and timed the diffusion over a given distance. Today, Livermore chemist Chris Hollars and physicist Ted Laurence are using laser light and fluorescing dyes to determine the diffusion of single molecules, ranging from small organic molecules less



(a) To image biological molecules with atomic resolution, Livermore physicist Henry Chapman and his team will inject single molecules into the beam of the x-ray free electron laser, irradiate each molecule with a blast of x-ray laser light, and record the resulting two-dimensional diffraction pattern before the molecule disintegrates. (b) A single three-dimensional image of a representative molecule will be constructed from terabyte data sets consisting of millions of diffraction patterns.

than a nanometer in diameter to large biomolecules 10 nanometers in diameter.

This LDRD project, led by Livermore physicist Daniel Barsky, combines molecular dynamics simulations with experiments to track the random walk of a protein "sliding clamp" as it scoots around a ring-shaped DNA molecule. Sliding clamps work much like a carabiner on a climbing rope and can "ride" more than 10,000 bases along a DNA double helix in less than a second. Interpreting the details of their zigzagging motions will help scientists understand the processes of DNA replication, recombination, and repair.

Hollars and Laurence are using single-molecule fluorescent resonance energy transfer (FRET) measurements to infer the speed and diffusional characteristics of an individual clamp protein as it moves. For the FRET measurements, scientists label a molecule with a photoluminescent "tag." Then they illuminate the molecule with laser light tuned to a specific wavelength, which causes the tag to fluoresce and give off light of a different wavelength. The laser beam is focused down to a volume of about 1 cubic micrometer, and the scientists watch for a DNA ring and clamp to diffuse into the volume. "We have a low concentration of DNA molecules in the mix, so we can view one molecule at a time," says Laurence.

Once a molecular complex arrives in the focus, the clamp fluoresces. If the clamp slides within 5 nanometers of the ring's labeled area while in the focus, the label absorbs the clamp's green photons and fluoresces red.

"The experiment," notes Hollars, "involves Brownian motion on two scales: the motion of the DNA ring as it dances through the volume, and the motion of the clamp as it slides around the ring."

Eventually, the team hopes to label multiple areas of the DNA loop with other fluorescent tags to provide an even more detailed picture of how the clamp moves around the DNA ring.

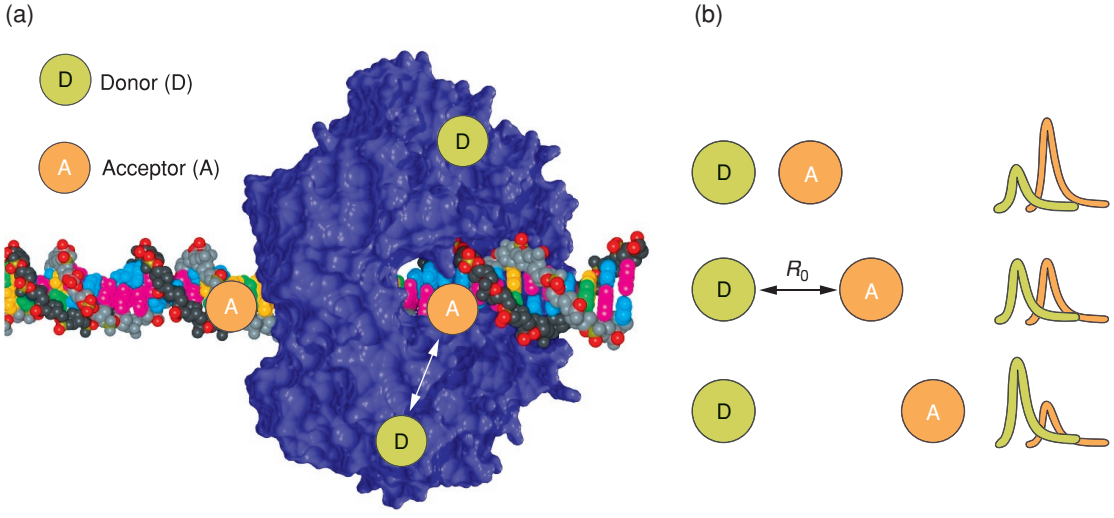
Bubble, Bubble, Toil, and Trouble

"Brownian motion is a beautiful example of Einstein's insight," says Livermore physicist Bill Wolfer. "He showed that by examining a particle moving in a gas or fluid, we can extract information on a physical aspect of that particle—the diffusion coefficient."

As it turns out, this property is of great importance in stockpile stewardship research, particularly for plutonium aging. When plutonium—or any radioactive material— decays, it generates helium atoms, which diffuse into small bubbles about 1.5 nanometers in diameter. These bubbles can affect the material's properties such as its strength.

To measure how much helium has been formed, scientists usually melt a material and extract the trapped helium, but this technique is too volatile for plutonium studies. "When we heat a material with bubbles of gas in it, the bubbles expand and eventually burst, sending material splattering everywhere," says Wolfer. "That is not an experiment we can conduct with plutonium."

Instead, to determine how the helium behaves when plutonium is heated to melting and beyond, Wolfer and chemical engineer Alison Kubota simulated the discrete motions of individual plutonium atoms and their interactions over time and at varying temperatures. Using the molecular dynamics code MDCASK, Kubota modeled the behavior of helium atoms in a block of aluminum as it was heated to the melting point. The simulations correctly yielded the diffusion coefficient and showed that a bubble will coalesce in about 1 nanosecond; two bubbles will diffuse and



Fluorescence resonance energy transfer (FRET) can be used to measure the distance between two labeled biomolecules. (a) When the two molecules are close together, the donor molecule in the proton clamp emits a photon of a given wavelength, which is absorbed by the second molecule in the DNA ring. (b) The strength of the two signals depends on the distance (R_0) between the donor and the acceptor. When the two are farther apart, only the donor wavelength is observed. When they are close together, the acceptor wavelength dominates.

touch in 680 nanoseconds and then fuse in 30 picoseconds. Says Kubota, "Brownian motion turns out to be the deciding factor in the process."

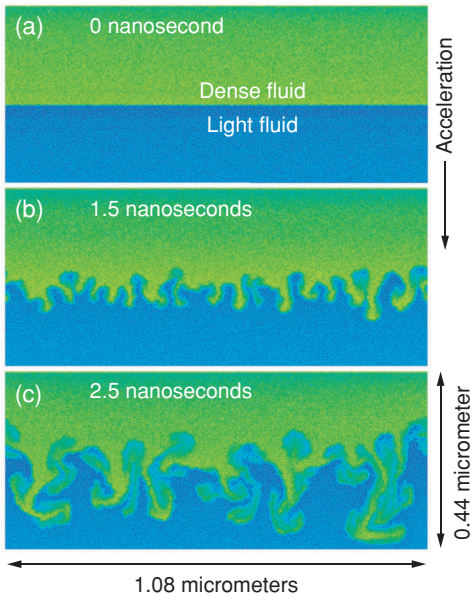
Yet, a bubble is not a solid pollen particle suspended in a liquid. Thus, Einstein's papers on Brownian motion turn out to be far more profound and transcend the explanation of the original experiments that inspired them. Brownian motion applies to any observable feature in a gaseous or fluid medium, such as interfaces between proteins and water, between a gas and a fluid in a bubble, or between two different fluids. In fact, bubbles diffuse because the bubble surface is subject to Brownian motion. The random motion of atoms along an interface between two different liquids also seeds hydrodynamic instabilities. This connection has long been accepted by scientists, but it had not been demonstrated until the recent work of Kubota in her LDRD project to model hydrodynamic instabilities at the atomic level.

Hydrodynamic instabilities are fluid phenomena involving the mixing between two fluids of different densities at the fluid interface, due to some external acceleration such as gravity. By simulating these instabilities in 3D, Kubota and her collaborators hope to obtain an atomic-scale view of phenomena and include those data in continuum-type fluid codes. "For instance, when we look at two fluids mixing, we often see bubbles," says Kubota, "but we have no idea how those bubbles affect the instabilities. Now, with these powerful codes and supercomputers, we can work it out from the most basic of Newton's laws."

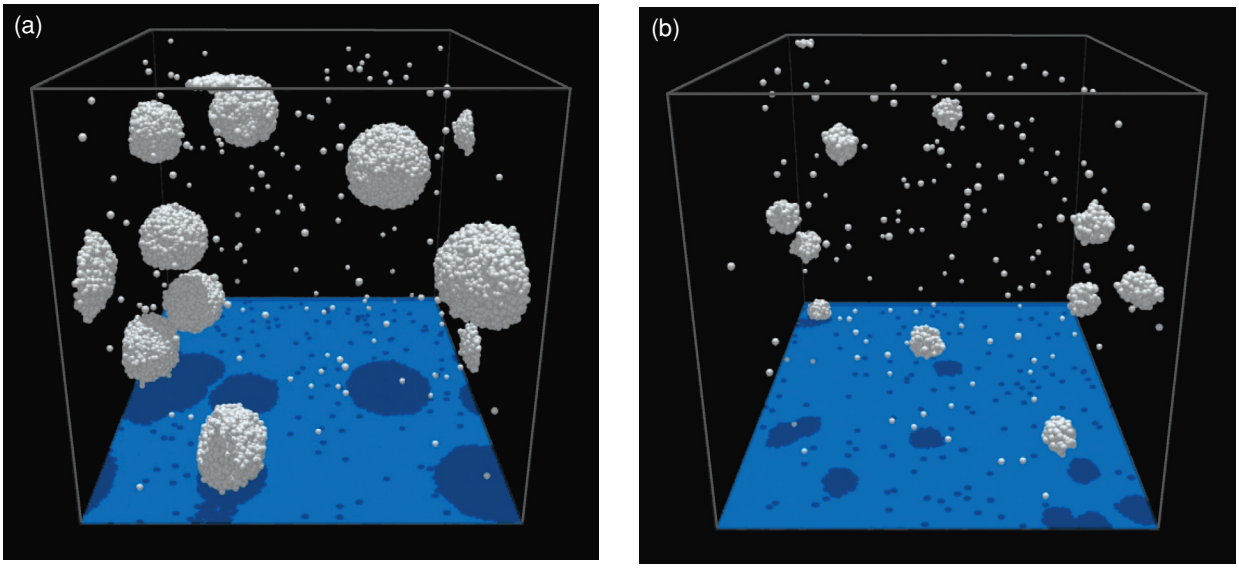
From First Principles

Another group at Lawrence Livermore is simulating the motion of atoms from first principles using the laws of quantum mechanics as their only input. The Quantum Simulations Group investigates material behavior at high temperatures and pressures, at the nanoscale, and in solution. Livermore physicist Giulia Galli, who leads the group, says, "Two of these areas in particular involve Brownian motion: materials in extreme conditions and materials in fluids."

Members of the group use first-principles molecular dynamics and quantum Monte Carlo codes to examine the motion of liquids at the microscopic level. Their projects, many of which are LDRD funded, include solving quantum mechanical



Hydrodynamic simulations of systems with millions of atoms are now possible at the atomic scale, given the increased power of supercomputer systems such as BlueGene/L and codes such as MDCASK. Sample results from a two-dimensional atomistic simulation of a Rayleigh–Taylor instability.



Models of helium atoms show how the atoms behave when a material is heated to the melting point: (a) 3,000 atoms forming bubbles at 4 nanometers, and (b) 200 atoms forming bubbles at 1.5 nanometers.

calculations for large numbers of atoms in a variety of physical conditions.

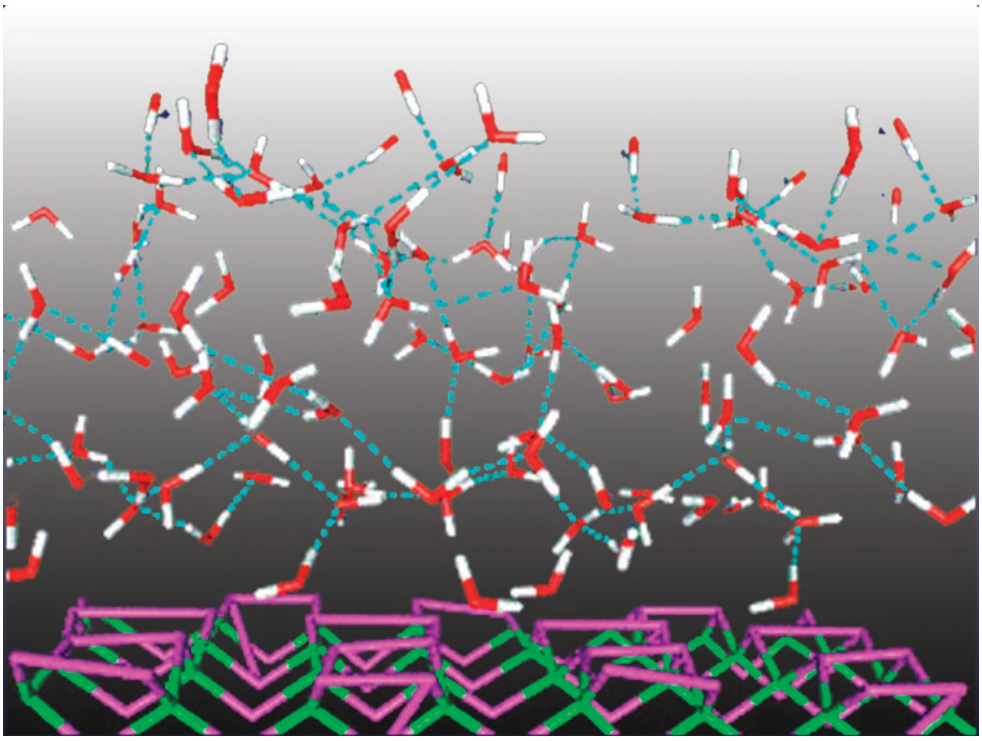
A recent success is the discovery of a new melt curve of hydrogen at extremely high pressures. (See *S&TR*, January/February 2005, pp. 4–13.) Results from these simulations provided strong evidence that a low-temperature quantum fluid may exist in hydrogen. The team is developing experimental measurements to help verify the existence of a maximum melting temperature and the transformation of solid molecular hydrogen to a metallic liquid at enormous pressures.

Molecular dynamics codes are also used to examine the behavior of water and its structural, dynamic, and electronic properties at the molecular level. "It may sound strange that now, at the beginning of the 21st century, scientists still don't completely understand the bonding of water both theoretically and experimentally," says Galli. The group is studying water under ambient conditions, under pressure, and in confined geometries to determine how its structure and electronic properties change as thermodynamic conditions vary.

The group's calculations point out the challenges that remain in understanding this abundant material. "At the nanoscale, predicting the behavior of water and aqueous solutions is extraordinarily challenging, and experimental data are still sparse," says Galli. "In this regime, classical simulations can become unreliable. Quantum simulations, in contrast, require no experimental input, so they can make accurate predictions."

One example of the group's work involves simulations of liquid–solid interfaces, particularly the diffusion of water on surfaces. Recent simulations show that water does not uniformly wet the surface of silicon carbide, a leading candidate semiconductor for biocompatible devices. Rather, water molecules prefer to bind along directions parallel to silicon atoms forming pairs (dimers) on the surface.

"We're following in Einstein's footsteps," says Galli. "In our calculations and simulations, we're using his concepts of Brownian motion at the atomic level, combined with computers now powerful enough to predict the motion of individual atoms, to build a greater understanding of our world as a whole."



Giancarlo Cicero, a postdoctoral researcher at Livermore, and his colleagues conducted quantum simulations of water on silicon carbide, allowing scientists to better understand the electronic, structural, and dynamic properties of the liquid–solid interface at the microscopic level.

It's Totally Random

Later in his life, Einstein became immersed in searching for a "theory of everything" and dismissed his work on Brownian motion as unimportant. However, random fluctuations and statistical mechanics are fundamental to the most elemental building blocks of the physical world and are called on to explain the mysterious processes of protein folding, cell-membrane function, evolution, and even stock market behavior. In demystifying Brownian motion, Einstein linked statistical mechanics to observable reality. At Lawrence Livermore, scientists continue to reap the rewards of his discovery and intuition.

—Ann Parker

Key Words: Albert Einstein, Brownian motion, fluid behavior, fluorescent resonance energy transfer (FRET), helium bubbles, hindered transport, hydrodynamic instabilities, lattice Boltzmann (LB) model, Markov chain Monte Carlo (MCMC) technique, molecular dynamics, quantum simulations, random walk, sequential Monte Carlo (SMC) technique, statistical mechanics, thermodynamics.

For information on Lawrence Livermore's activities for the World Year of Physics, see www.llnl.gov/pao/WYOP.